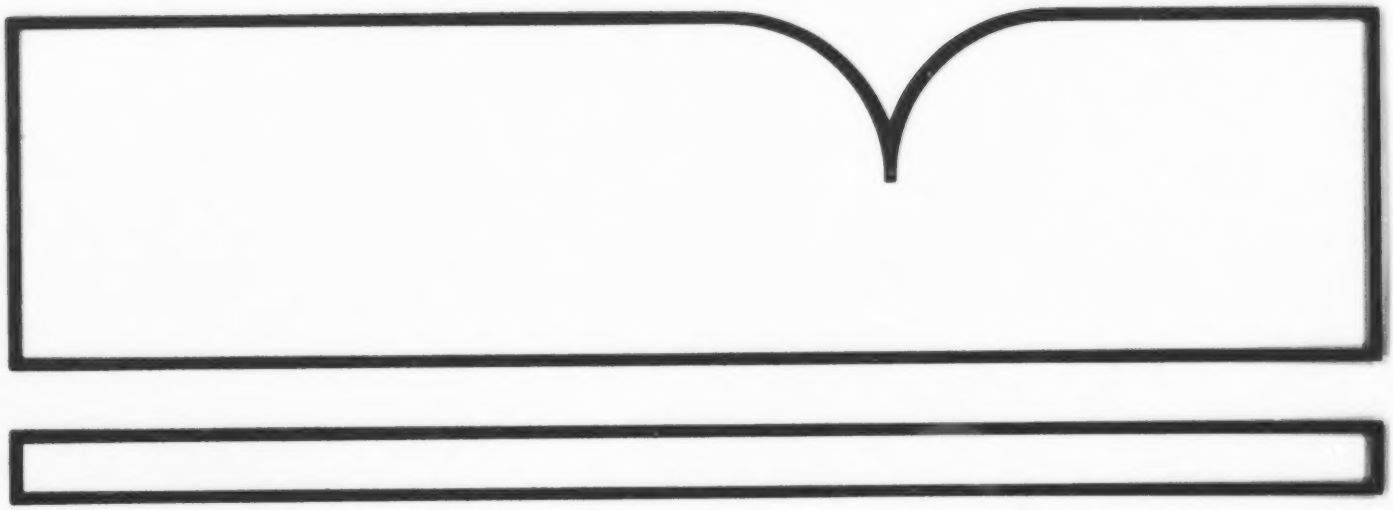
PB86-119070

Chemistry and Corrosiveness of Dew

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

Oct 85



U.S. Department of Commerce
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NTIS

PB86-119070

EPA/600/D-85/259
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NATIONAL TECHNICAL
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U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA/600/D-85/259		PB86 119070/AS

4. TITLE AND SUBTITLE	5. REPORT DATE
CHEMISTRY AND CORROSIVENESS OF DEW	October 1985
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
William E. Wilson, E.O. Edney and D.C. Stiles	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
	CCVN1A-09/3140 (FY85)
	11. CONTRACT/GRANT NO.
(Same as Box 12)	
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Atmospheric Sciences Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711	14. SPONSORING AGENCY CODE EPA/600/09

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Increased attention has been given recently to the impact of the deposition of acidic species on the degradation of commercially important materials such as metals and paints. Although it has been appreciatd for some time that air pollutants, especially SO_2, can accelerate atmospheric corrosion and erosion processes, it has only been in the past few years that an aggressive effort has been made to develop damage functions that can be employed to predict the extent of corrosion or erosion for a given set of environmental conditions. To date all of the damage functions have been generated by conducting regression analyses on corrosion data obtained from field studies. These types of analyses have shed some light on which environmental factors play major roles in accelerating the degradation process above that expected due to natural weathering. In particular, it has been established that the ambient SO_2 concentration and the time the exposed surfaces are wet play important roles in the corrosion rate of metals. However these damage functions are phenomenological models and their application to environmental conditions other than those from which they were derived may produce erroneous results. In order to evaluate the economic impact of various control strategies, reliable damage functions must be developed to predict the impact of a reduction in ambient SO_2 concentration or the pH of the rain on the degradation process.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	6
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	$9.95

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

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Increased attention has been given recently to the impact of the deposition of acidic species on the degradation of commercially important materials such as metals and paints. Although it has been appreciated for some time that air pollutants, especially SO_2, can accelerate atmospheric corrosion and erosion processes, it has only been in the past few years that an aggressive effort has been made to develop damage functions that can be employed to predict the extent of corrosion or erosion for a given set of environmental conditions. To date all of the damage funtions have been generated by conducting regression analyses on corrosion data obtained from field studies. These types of analyses have shed some light on which environmental factors play major roles in accelerating the degradation process above that expected due to natural weathering. In particular, it has been established that the ambient SO_2 concentration and the time the exposed surfaces are wet play important roles in the corrosion rate of metals. However these damage functions are phenomenological models and their application to environmental conditions other than those from which they were derived may produce erroneous results. In order to evaluate the economic impact of various control strategies, reliable damage functions must be developed to predict the impact of a reduction in ambient SO_2 concentration or the pH of the rain on the degradation process.

As a first step in the development of such models we have conducted a series of laboratory experiments to clarify the role of a number of air pollutants in the atmospheric corrosion of galvanized steel, a commercially important metal alloy used extensively throughout the United States. In particular, we focus on the corrosion of galvanized steel in the presence of dew. Experiments were conducted where galvanized steel was exposed to air matrices that contained the following mixtures: (1) SO_2, (2) NO_2, (3) irradiated C_3H_6/NO_x, and (4) irradiated $C_3H_6/NO_x/SO_2$. During the short-term exposures dew was produced periodically on the test panels, collected and analyzed for its chemical contents. The focus of this work was on the composition of the soluble corrosion products.

Figure 1 illustrates the exposure system which consists of two exposure chambers in parallel coupled to an 11.3-m^3 aluminum smog chamber that is operated as a continuous stirred tank reactor and serves as a resevoir for the exposure chambers. Steam is injected into the chamber by the dew point control system that is programmed to maintain a constant value for the dew point. The exposure chambers are constructed of clean Teflon glued to a 13-cm x 13-cm x 152-cm aluminum frame. Each chamber has seven positions for monitoring test panels and each position has a chiler back plate with supplied coolant so that the panel can be chilled below the air dew point to produce dew in sufficient quantity to drop into the collection through below each panel. Blowers are mounted on the exposure chambers to maintain turbulent conditions and the blower settings were adjusted to produce wind speeds of 300 cm/sec. Additional information concerning the operation of the

exposure system and its associated gas monitors are presented elsewhere [1,2].

The experimental protocol consisted of first bringing the contents of the mixture to steady state. The galvanized steel panels were cleaned according to ASTM procedures and placed into the exposure chambers. The control system was programmed to generate a series of dew/dry samples. Each dew/dry cycle consisted of 7 h of dew formation followed by 5 h with the panel temperatures above the air dew point. At the end of the experiments the collected dew was analyzed for Zn by atomic absorption spectroscopy, HCHO by chromotropic acid, and its anionic contents by ion chromatography.

The amount of compound that deposits into the dew and its deposition velocity were calculated by using the difference in the gas phase concentrations during the dry and dew periods or by employing the concentration of the compound in the dew and the volume of dew. Deposition to a dry panel can occur, but, for the majority of the compounds studied most of the deposition took place in the presence of dew.

Short-term SO_2 experiments were conducted at SO_2 concentrations of 3,7,30,45,95,240 and 650 ppb. SO_2 deposition was greatly enhanced in the presence of dew. The average deposition velocity during periods of wetness was 0.9 cm/sec. Analysis of dry panels suggested that, in the absence of dew, saturation occurs and the saturation density is consistent with the presence of a monolayer of absorbed SO_2. Regression analysis of the Zn and $SO_4^=$ dew molar concentrations for all exposure experiments yielded a 1:1 relationship between the two species. However, examination of the chemical composition of the dew for the 3 and 7 ppb SO_2 experiments showed the presence of excess Zn (50-100μM). The excess Zn concentration is similar in magnitude to the solubility of $ZnCO_3$ (79.4μM at T=15°C). $ZnCO_3$ is a corrosion product that is formed on galvanized steel under clean air conditions.

Experimental results from the 500 ppb NO_2 exposure showed that even in the presence of dew NO_2 was not readily deposited (v_d = 0.05 cm/sec) and suggest that the deposition is controlled by the effective surface resistance rather than the gas phase resistance. The dominant NO_x^- species formed in the dew was NO_2^-, however, it was not possible to determine its impact on the corrosion of dew because the extent of corrosion that might have been associated with deposited NO_x was similar in magnitude to the solubility of $ZnCO_3$ discussed above.

Galvanized steel panels were exposed to an irradiated C_3H_6/NO_x mixture (residence time = 2 h). NO_2^-, NO_3^-, HCHO and Zn were detected in the dew. The source of dew NO_3^- was most likely the deposition of HNO_3 whereas the small amounts of NO_2^- found arose from the deposition of HONO or PAN. The estimated dry deposition velocity for HCHO in the presence of dew based on the decrease in the gas phase decrease was 0.9 cm/sec. The deposition velocity based on the dew HCHO concentration obtained using the chromotropic acid method was 0.3 cm/sec. These results suggest that some of the deposited HCHO was converted to $CHOO^-$ and that the major chemical constituent in the dew was $Zn(CHOO)_2$. These findings are in agreement with those of KnotKova who found that aqueous HCHO was converted to $CHOO^-$ in the presence of galvanized steel and, in addition, accelerated the corrosion process. [3]

NO_2^-, NO_3^-, HCHO, $SO_3^=$, $SO_4^=$ and Zn were found in dew samples collected during the $C_3H_6/NO_x/SO_2$ irradiation (residence time = 2 h) experiment. The dominant sulfur compound in the dew was $SO_3^=$ whose concentration was approximately equal to the agueous HCHO concentration which suggests that the $HCHOHSO_3^-$ adduct was formed in the dew. The relative Zn, HCHO, and $SO_3^=$ dew concentrations found suggests that Zn reacts with the $HCHOHSO_3^-$ adduct rather than with the dissolved SO_2 or HCHO. In this experiment good agreement was found between the HCHO deposition velocity obtained using the change in the gas phase concentrations and that found by dew analysis.

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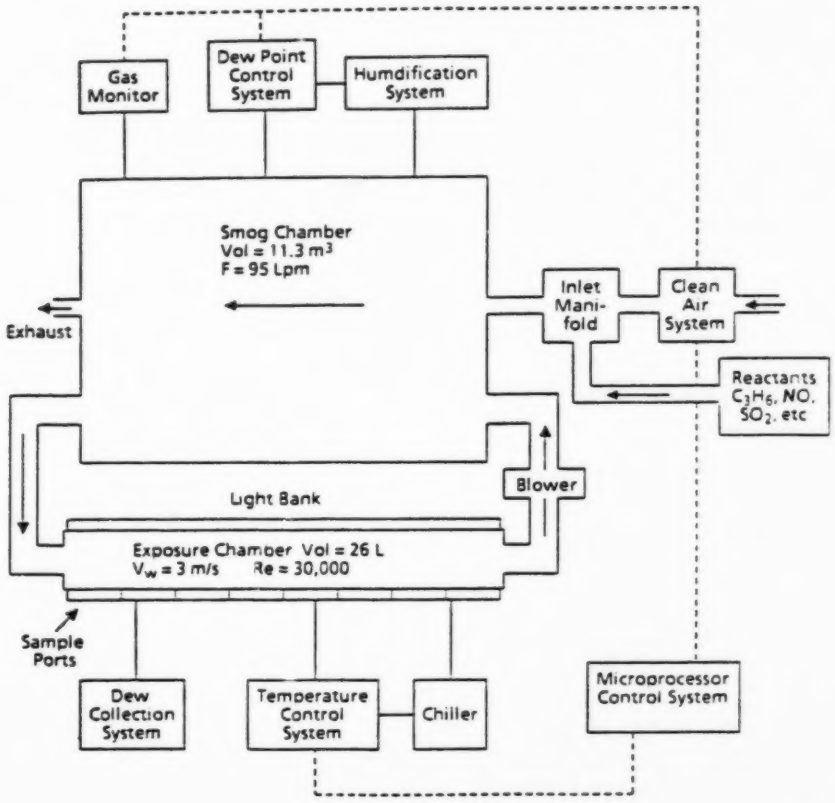

Figure 1. Schematic of Exposure System.